



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 41/14, 43/12, 41/01, 17/361 // 45/42, 49/167, 49/457	A1	(11) International Publication Number: WO 99/37598 (43) International Publication Date: 29 July 1999 (29.07.99)
(21) International Application Number: PCT/US98/10437 (22) International Filing Date: 22 May 1998 (22.05.98) (30) Priority Data: 09/012,959 26 January 1998 (26.01.98) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: BEHR, Frederick, E.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). CHEBURKOV, Yuri; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: SCHULTE, Daniel, C. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: PROCESS FOR PREPARING HYDROFLUOROETHERS (57) Abstract Described is a reaction of a fluorinated alkoxide with an alkyl fluorovinylalkyl ether, the alkyl fluorovinylalkyl ether having alpha-beta carbon-carbon unsaturation relative to the ether oxygen, to produce a hydrofluoroether.		

PROCESS FOR PREPARING HYDROFLUOROETHERS

Field of the Invention

The invention relates to reaction of a fluorinated alkoxide with an alkyl
5 fluorovinylalkyl ether to prepare a hydrofluoroether.

Background

Hydrofluoroethers (HFEs) are a class of commercially valuable chemical
compounds. In a number of applications hydrofluoroethers have been found to be
10 useful replacements for chlorofluorocarbons (CFCs), the use of which is presently
disfavored and regulated due to the adverse effects CFCs are believed to have on
the environment. Hydrofluoroethers have been found to be less harmful to the
earth's ozone layer than CFCs because, for one thing, they are typically more easily
degraded within the earth's atmosphere (they exhibit a low "ozone depletion
15 potential").

Hydrofluoroethers have been found to be useful in a number of important
industrial and commercial applications. They can be used alone or in combination
with other chemicals, e.g., in applications where CFCs have been used in the past
(as a solvent, a cleaning fluid, a polymerization medium, a fire extinguishing
20 medium, a heat transfer agent, a refrigerant, or as a metal working agent in the
cutting or forming of metals). With increasing demand for hydrofluoroethers, there
exists an ongoing need to identify efficient methods for their production.

Hydrofluorocarbons (HFCs), which include a very wide variety of organic
compounds composed of hydrogen, fluorine, and carbon, are also important
25 industrial and commercial chemicals for use in applications such as in fire-fighting
compositions, gaseous dielectrics, sterilant carriers, refrigerants, heat transfer fluids,
cleaning fluids, and solvent applications, etc. As a single example, HFC-236
($C_3F_6H_2$) is useful as a refrigerant as a replacement for CFC-11, CFC-113 and CFC-
114. There is continuing need for efficient methods of preparing a variety of
30 different commercially useful HFCs such as HFC-236.

Summary of the Invention

The present invention provides a method of reacting a fluorinated alkoxide with an alkyl fluorovinylalkyl ether. According to the invention, a fluorinated alkoxide can be reacted with a fluorinated vinyl ether to produce a
5 hydrofluoroether. At the same time can be produced a conjugate base of a fluorinated carbonyl compound which may be further processed to produce other useful chemical compounds (e.g., hydrofluorocarbons). Thus, the inventive method provides not only a method of producing valuable and useful hydrofluoroethers, but at the same time can provide fluorinated carbonyl compounds that can be further
10 reacted to produce other useful chemical compounds such as hydrofluorocarbons. The invention allows two classes of useful compounds to be produced, achieving efficiencies that could not be met by methods in the prior art.

An aspect of the invention relates to the reaction of a fluorinated alkoxide with an alkyl fluorovinylalkyl ether having alpha-beta carbon-carbon unsaturation
15 relative to the ether oxygen, to produce a hydrofluoroether. The resultant hydrofluoroether can be of any chemical identity, and will depend upon the chosen reactants.

Another aspect of the invention relates to a process for preparing a hydrofluoroether. The process includes the steps of providing an alkyl
20 fluorovinylalkyl ether; providing a fluorinated alkoxide; and reacting the alkyl fluorovinylalkyl ether with the fluorinated alkoxide to produce a hydrofluoroether.

A specific embodiment of the invention relates to a process for preparing a hydrofluoroether and a hydrofluorocarbon. The process includes the steps of providing an alkyl fluorovinylalkyl ether; providing a fluorinated alkoxide; reacting
25 the alkyl fluorovinylalkyl ether with the fluorinated alkoxide to produce a hydrofluoroether and a conjugate base of a fluorinated carbonyl compound; treating the conjugate base of the fluorinated carbonyl compound with water to produce an alpha-hydro carbonyl compound; and, if the alpha-hydro carbonyl compound comprises a carboxylic acid, decarboxylating the alpha-hydro carbonyl compound to
30 form a hydrofluorocarbon.

Within the present description, the following terms will be given the designated meanings:

“Fluorinated,” as in fluorinated aliphatic, and the prefix “fluoro-,” as in fluorovinylalkyl, refer to organic chemical moieties in which at least one carbon-bonded hydrogen atom has been replaced by fluorine.

“perfluorinated” and the prefix “perfluoroalkyl-” refer to organic chemical moieties in which essentially all carbon-bonded hydrogen atoms in an alkyl group have been replaced by fluorine atoms, e.g., at least 95 percent, preferably at least 99 percent, of all hydrogen atoms have been replaced with fluorine.

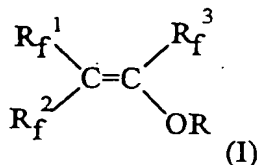
“hydrofluorocarbon” refers to compounds composed of carbon, hydrogen and fluorine atoms.

“hydrofluoroether” and “HFE” refer to fluoroalkyl-alkyl ether compounds.

Detailed Description

According to the invention, an alkyl fluorovinylalkyl ether can be reacted with a fluorinated alkoxide to produce a hydrofluoroether.

The alkyl fluorovinylalkyl ether can be any ether compound comprising an ether-bonded alkyl component (R) and an ether-bonded fluorovinylalkyl component, where the ether-bonded fluorovinylalkyl component includes carbon-carbon unsaturation between the alpha and beta carbons (alpha-beta unsaturation) relative to the ether oxygen. Examples of such alkyl fluorovinylalkyl ether compounds include those of general formula I:

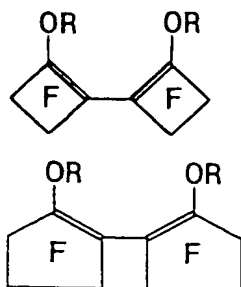
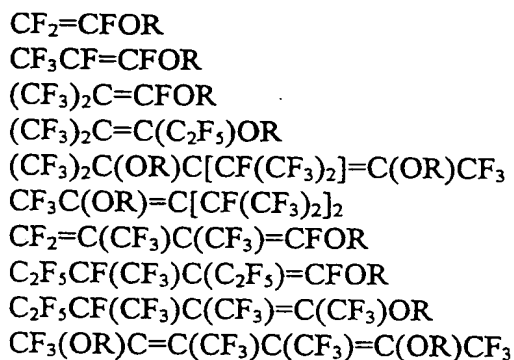


In formula I, R_f^1 , R_f^2 and R_f^3 are independently fluorine atoms or fluorinated aliphatic groups preferably having from 1 to 10 carbon atoms which may be linear, branched, or cyclic, and which may optionally contain a catenary ether oxygen atom, or be unsaturated. R can be any alkyl that is sufficiently sterically unhindered to allow reaction with a fluorinated alkoxide. Preferably R_f^1 , R_f^2 , and R_f^3 are each,

independently, F or a perfluorinated aliphatic group having from 1 to 10 carbon atoms, and which may be linear, branched, or cyclic, and which may optionally contain a catenary ether oxygen atom. R is preferably a linear or branched alkyl having from 1 to 6 carbon atoms, and preferably having a non-tertiary carbon atom bonded directly to the ether oxygen. Also optionally, the alkyl fluorovinylalkyl ether can be di-functional with respect to the vinyl moiety, i.e., a bis-vinyl ether; in such instance a resulting carbonyl compound reaction product (see below) can be a bis-carbonyl compound.

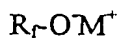
Alkyl fluorovinylalkyl ethers can be prepared by known methods. One such method is the addition of an alcohol to a fluoroalkene, followed by dehydrofluorination of the intermediate addition product. See M. Hudlicky, Chemistry of Organic Fluorine Compounds, pp. 285-9 and 409 (2nd ed. 1992). Preferred alkyl fluorovinylalkyl ethers can be derived from PFIB (octafluoroisobutylene) and lower alcohols (e.g., ethanol or methanol) as described by Koshar et al., J. Am. Chem. Soc., 79, 1741 (1957).

Some examples of useful alkyl fluorovinylalkyl ethers include the following:



wherein each R is independently an alkyl group preferably having from about 1 to 10, more preferably from about 1 to 6 carbons.

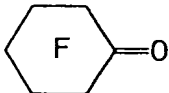
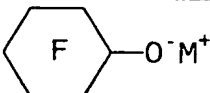
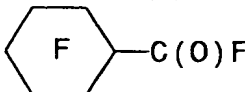
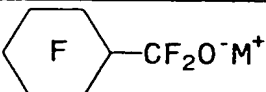
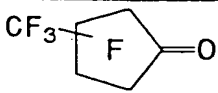
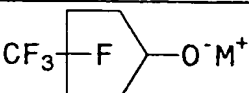
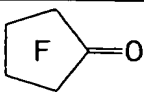
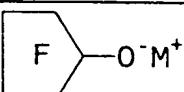
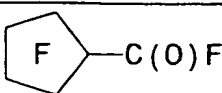
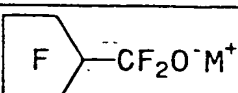
The fluorinated alkoxide can be any fluorinated alkoxide capable of reacting with the alkyl fluorovinylalkyl ether. An example of useful fluorinated alkoxides include those of general formula II:

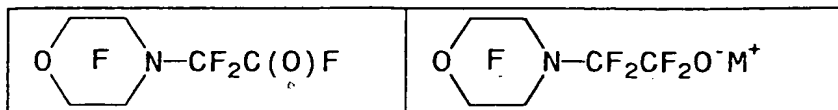


(II).

In formula II, M^+ describes a cation such as Na^+ , K^+ , Li^+ , NR_4^+ (wherein R comprises, e.g., a lower alkyl), etc., and R_f can be a linear or branched fluoroaliphatic group preferably having from 1 to 10 carbon atoms, optionally containing a catenary ether oxygen or trivalent nitrogen, and preferably being perfluorinated.

The fluorinated alkoxide can be derived from a fluorinated alkoxide precursor, (also referred to herein as "the precursor") as is well known in the chemical art, and according to a number of different, known methods. A number of exemplary fluorinated alkoxide precursors and corresponding fluorinated alkoxides are shown below:

Precursor	Fluorinated Alkoxide
$CF_2(O)$	CF_3OM^+
$CF_3C(O)F$	$C_2F_5OM^+$
$C_2F_5C(O)F$	$C_3F_7OM^+$
$C_3F_7C(O)F$	$C_4F_9OM^+$
$C_4F_9C(O)F$	$C_5F_{11}OM^+$
$C_5F_{11}C(O)F$	$C_6F_{13}OM^+$
$CF_3OCF_2C(O)F$	$CF_3OC_2F_4OM^+$
$(CF_3)_2C(O)$	$(CF_3)_2CFOM^+$
$(CF_3)_2NCF_2C(O)F$	$(CF_3)_2NCF_2CF_2OM^+$
$FC(O)CF_2C(O)F$	$M^+OC_3F_6OM^+$
	
	
	
	
	



According to one method of preparing a fluorinated alkoxide from a precursor, any of a fluorinated acyl fluoride, fluorinated acyl chloride, fluoroalkyl ester, a fluorinated anhydride, or a fluoroalkyl carbonate can be used as a suitable fluorinated alkoxide precursor (if a fluoroalkyl ester is used as a fluorinated alkoxide precursor, the carbon atom alpha to the ester oxygen should generally be at least di-fluorinated). These precursors can be converted to fluorinated alkoxides by contacting them with fluoride ion, e.g., in the form of an anhydrous alkali metal fluoride salt, in an anhydrous, polar, aprotic solvent, to generate a fluorinated alkoxide $\text{R}_f\text{-O}^-$ (the fluorinated alkoxide typically exists in solution in an ionic form, $\text{R}_f\text{-O}^-$). The fluoride ion can generally be reacted with the precursor in a stoichiometric amount, or perhaps a slight excess; a large excess of fluoride ion is undesirable due to the possibility that it be present to react with the alkyl fluorovinylalkyl ether.

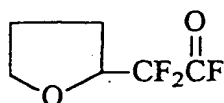
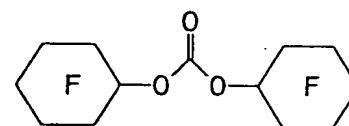
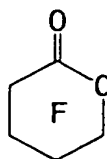
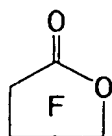
As a single example, a fluorinated acyl fluoride can be reacted with potassium fluoride to produce a corresponding fluorinated alkoxide, as follows:



- R_f' can be a linear or branched fluoroaliphatic group. R_f' preferably has from 1 to 6 carbon atoms. In the above reaction scheme, $\text{R}_f'\text{CF}_2^-$ in the fluorinated alkoxide corresponds to the group defined in formula II as R_f .

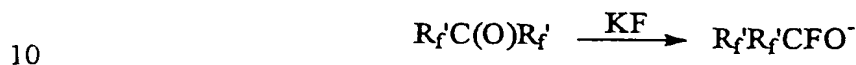
Examples of compounds that can be useful as fluorinated alkoxide precursors include fluorinated acyl fluorides, fluorinated acyl chlorides, fluoroalkyl esters, fluorinated anhydrides, and fluoroalkyl carbonates, and are exemplified as follows: $\text{CF}_3\text{C}(\text{O})\text{F}$, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{F}$, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{F}$, $\text{C}_4\text{F}_9\text{C}(\text{O})\text{F}$, $\text{C}_5\text{F}_{11}\text{C}(\text{O})\text{F}$, $\text{CF}_3\text{C}(\text{O})\text{Cl}$, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{Cl}$, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{Cl}$, $\text{C}_4\text{F}_9\text{C}(\text{O})\text{Cl}$, $\text{C}_5\text{F}_{11}\text{C}(\text{O})\text{Cl}$, $\text{CF}_3\text{CO}_2\text{CF}_3$, $\text{C}_2\text{F}_5\text{CO}_2\text{C}_2\text{F}_5$, $\text{C}_3\text{F}_7\text{CO}_2\text{C}_3\text{F}_7$, $\text{C}_4\text{F}_9\text{CO}_2\text{C}_4\text{F}_9$, $\text{C}_5\text{F}_{11}\text{CO}_2\text{C}_5\text{F}_{11}$, $\text{CF}_3\text{C}(\text{O})-\text{O}-\text{C}(\text{O})\text{CF}_3$, $\text{C}_2\text{F}_5\text{C}(\text{O})-\text{O}-$

$C(O)C_2F_5$, $C_3F_7C(O)-O-C(O)C_3F_7$, $C_4F_9C(O)-O-C(O)C_4F_9$, $C_3F_{11}C(O)-O-C(O)C_5F_{11}$, $CF_3OC(O)OCF_3$, $CF_3CF_2OC(O)OCF_2CF_3$, $C_3F_7OC(O)OC_3F_7$, etc.,



as well as partially fluorinated analogues thereof.

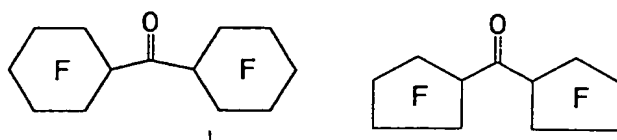
- 5 In a second method of producing a useful fluorinated alkoxide, a fluorinated alkoxide can be derived from a fluoroketone. A fluoroketone can be converted to a fluorinated alkoxide by reaction with a stoichiometric amount (or a slight excess, as described above) of anhydrous alkali metal fluoride to generate a secondary fluoroalkoxide.



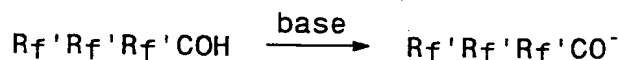
- Each R_f' can independently be as defined above. It can be preferred that in the ketone precursor, at least one of the R_f' groups have a primary carbon atom alpha to the carbonyl. Most preferably with respect to ketone fluorinated alkoxide precursors, one of the R_f' groups is $-CF_3$. With respect to the above reaction scheme, $R_f'R_f'CF-$ corresponds to the group defined in formula II as R_f .
- 15

Fluoroketones can be prepared, e.g., by methods described in M. Hudlicky, Chemistry of Organic Fluorine Compounds, pp. 62, 360-1, 380, 389, 392, 505, 617, and 654-7 (2nd ed. 1992).

- 20 Examples of fluoroketones useful as fluorinated alkoxide precursors include, for example: $CF_3C(O)CF_3$, $C_2F_5C(O)C_2F_5$, $C_3F_7C(O)C_3F_7$, $C_4F_9C(O)C_4F_9$, $C_4F_9C(O)CF_3$, $HC_4F_8C(O)CF_3$,



A fluorinated alkoxide can also be prepared by reacting a fluorinated tertiary alcohol fluorinated alkoxide precursor with a stoichiometric amount (or slight excess) of base, e.g., potassium hydroxide or sodium hydride, in a polar, aprotic solvent, to produce a tertiary fluorinated alkoxide:



Each R_f' can independently be a linear or branched fluoroaliphatic group, preferably having from about 1 to 6 carbon atoms. In this reaction scheme $R_f' R_f' R_f' C-$ corresponds to the group defined in formula II as R_f .

10 Examples of suitable tertiary alcohols for use as precursors to a fluorinated alkoxide include $(CF_3)_3COH$, $(CF_3)_2C(C_2F_5)OH$, and $(CF_3)_2CFCF_2C(CF_3)_2OH$.

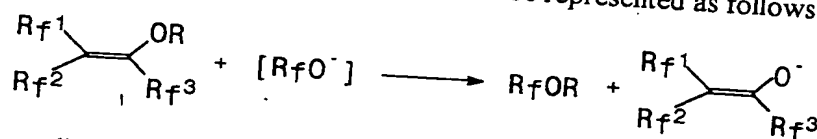
Fluorinated acyl fluorides are well known in the chemical art, and can be prepared by electrochemical fluorination (ECF) of a corresponding hydrocarbon carboxylic acid (or a derivative thereof), using either anhydrous hydrogen fluoride (Simons ECF) or $KF \cdot 2HF$ (Phillips ECF) as the electrolyte. Fluoroalkyl esters and fluoroalkyl carbonates are also well known in the chemical art, and can be prepared from fluorinated acyl fluorides, or can be directly prepared by known methods such as fluorination of an appropriate organic precursor.

20 Fluorinated acyl fluorides and fluorinated ketones can also be prepared by dissociation of fluorinated carboxylic acid esters, which can be prepared from a hydrocarbon or partially-fluorinated carboxylic acid ester by direct fluorination with fluorine gas. Dissociation can be achieved by contacting the fluorinated carboxylic acid ester with a source of fluoride ion (see, e.g., United States Patent No. 3,900,372 (Childs) or by combining the ester with an initiating reagent such as a gaseous non-hydroxylic nucleophile, a liquid non-hydroxylic nucleophile, or a mixture of at least one non-hydroxylic nucleophile (gaseous, liquid, or solid) and at

least one solvent which is inert to acylating agents. See also United States Patent 5,466,877 (Moore).

Suitable anhydrous polar aprotic solvents for use in the above reactions include acyclic ethers such as diethyl ether, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether; carboxylic acid esters such as methyl formate, ethyl formate, methyl acetate, diethyl carbonate, and propylene carbonate; alkyl nitriles such as acetonitrile; alkyl amides such as N,N-diethylformamide, and N-methylpyrrolidone; alkyl sulfoxides such as dimethyl sulfoxide; alkyl sulfones such as dimethylsulfone, tetramethylene sulfone, and other sulfolanes; oxazolidones such as N-methyl-2-oxazolidone; and mixtures thereof.

An example of the inventive reaction can be represented as follows:



wherein an alkyl fluoroalkylvinyl ether is reacted with a fluorinated alkoxide to produce a hydrofluoroether and a conjugate base of a fluorinated carbonyl compound. In the above reaction scheme each of R_f , R_f^1 , R_f^2 , R_f^3 , and R are as defined.

The reaction may be accomplished by preparing a reaction solution comprising the alkyl fluorovinylalkyl ether and the fluorinated alkoxide. The reaction can be carried out in any suitable reaction vessel, at ambient (e.g., atmospheric) pressure, although when volatile reactants are used or when volatile products are produced a pressure vessel can be preferred.

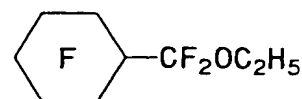
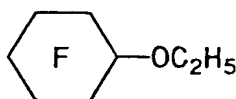
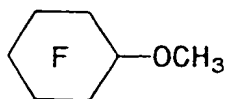
The amounts of the alkyl fluorovinylalkyl ether and fluorinated alkoxide reactants can be chosen as desired, but generally, for monovalent ether reactants the relative molar amounts of each reactant can be within a range from about a 1:1 molar ratio of alkyl fluorovinylalkyl ether to fluorinated alkoxide, to a 1:2 ratio. Similarly, for bis-alkyl fluorovinylalkyl ether reactants the molar ratio can preferably be in the range from about 1:1 to 1:4, bis-alkyl fluorovinylalkyl ether to fluorinated alkoxide.

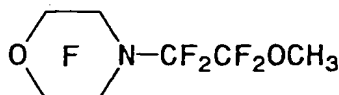
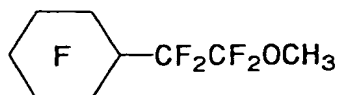
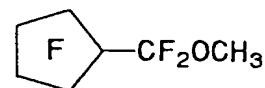
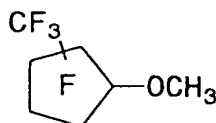
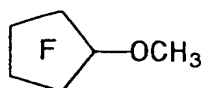
Generally, heating of the reaction solution is not necessary, and the reaction can proceed at ambient temperature. Still, any temperature between 0 °C and

100°C may be used, with ambient temperature being preferred. Mild heating e.g., to about 60°C, can be useful to cause production of a fluorinated alkoxide from its precursor, or to increase reaction rate of the alkyl fluorovinylalkyl ether and the fluorinated alkoxide. The course of the reaction can be monitored using standard analytical techniques, e.g., gas chromatography, to observe conversion of the reactants and product formation.

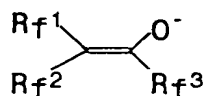
In a preferred method of the process of the invention, the fluorinated alkoxide can be initially generated *in situ*, i.e., within the reaction solution, for example, by adding a source of anhydrous fluoride ion, or a base, as appropriate, to a fluorinated alkoxide precursor dissolved in solvent (with mild heating if desired). Thereafter, the alkyl fluorovinylalkyl ether can be added to the reaction solution. The reactants may be charged at a temperature at or below room temperature (25°C), and then warmed slightly to effect formation of the fluorinated alkoxide. The reaction solution may then be cooled to allow addition of the alkyl fluorovinylalkyl ether to the reactor.

A reaction product can include a hydrofluoroether having the structure R_f-O-R , wherein R_f and R are as defined. Examples of a number of hydrofluoroethers are described, for example, in Assignee's copending United States patent application serial number 08/649,361, having Attorney's Docket Number 51258USA4C, and filed May 17, 1996. A number of specific, non-limiting examples of HFEs that can be prepared by the reaction include $C_3F_7OCH_3$, $C_3F_7OC_2H_5$, $C_3F_7OC_3H_7$, $C_3F_7OC_4H_9$, $C_3F_7OC_5H_{11}$, $C_3F_7OC_6H_{13}$, $C_4F_9OCH_3$, $C_4F_9OC_2H_5$, $C_4F_9OC_3H_7$, $C_4F_9OC_4H_9$, $C_4F_9OC_5H_{11}$, $C_4F_9OC_6H_{13}$, $C_5F_{11}OCH_3$, $C_5F_{11}OC_2H_5$, $C_5F_{11}OC_3H_7$, $C_5F_{11}OC_4H_9$, $C_5F_{11}OC_5H_{11}$, $C_5F_{11}OC_6H_{13}$, $C_6F_{13}OCH_3$, $C_6F_{13}OC_2H_5$, $C_6F_{13}OC_3H_7$, $C_6F_{13}OC_4H_9$, $C_6F_{13}OC_5H_{11}$, $C_6F_{13}OC_6H_{13}$, $C_7F_{15}OCH_3$, $C_7F_{15}OC_2H_5$, $C_7F_{15}OC_3H_7$, $C_7F_{15}OC_4H_9$, $C_7F_{15}OC_5H_{11}$, $C_7F_{15}OC_6H_{13}$, $C_8F_{17}OCH_3$, $C_8F_{17}OC_2H_5$, $C_8F_{17}OC_3H_7$, $C_8F_{17}OC_4H_9$, $C_8F_{17}OC_5H_{11}$, $C_8F_{17}OC_6H_{13}$, $CF_3OC_3F_6OCH_3$, $C_2F_5OC_2F_4OC_2H_5$, $CH_3OC_4F_8OCH_3$





Another reaction product can be a conjugate base of a fluorinated carbonyl compound having the mesomeric carbanion structure:

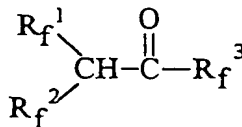


- 5 (This structure is shown without the presence of a stabilizing counterion, e.g., M^+ as previously defined). In the above formula, the identities of the R_f^1 , R_f^2 , and R_f^3 groups depend on the chemical identity of the alkyl fluorovinylalkyl ether reactant.

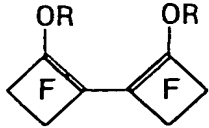
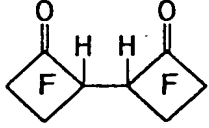
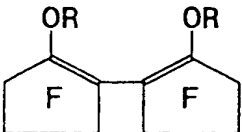
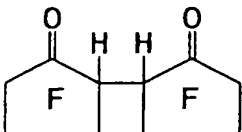
The immediate hydrofluoroether and conjugate base reaction products can be separated, and each can be individually processed or further reacted, as desired.

- 10 Because the conjugate base reaction product exists as a non-volatile salt, while the hydrofluoroether is typically relatively more volatile, separation and isolation of the hydrofluoroether from the reaction solution can generally be accomplished by simple distillation or nitrogen purge methods.

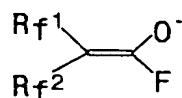
15 Once the hydrofluoroether has been separated from the reaction solution, the conjugate base of the fluorinated carbonyl compound can be further processed or reacted to produce other useful and desired chemical compounds. For example, the conjugate base can be treated with water to produce an alpha-hydro carbonyl compound. If R_f^3 is a fluoroalkyl, the conjugate base of the fluorinated carbonyl compound reaction product will be a conjugate base of a fluoroketone. Upon
20 treatment with water such a compound can yield an alpha-hydro fluoroketone.



Exemplary alpha-hydro fluoroketones are shown in the table below with their corresponding alkyl fluorovinylalkyl ether reactants.

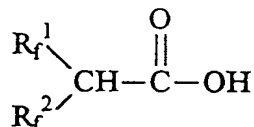
alkyl fluorovinylalkyl ether reactant	fluorinated carbonyl compound
$(CF_3)_2C=C(C_2F_5)OR$	$(CF_3)_2CHC(O)C_2F_5$
$(CF_3)_2C(OR)C[CF(CF_3)_2]=C(OR)CF_3$	$(CF_3)_2C(OR)CH[(CF(CF_3)_2)]C(O)CF_3$
$CF_3C(OR)=C[CF(CF_3)_2]_2$	$CF_3C(O)CH[CF(CF_3)_2]_2$
$CF_2=C(CF_3)C(CF_3)=CFOR$	$CF_2=C(CF_3)CH(CF_3)C(O)F$
$C_2F_5CF(CF_3)C(C_2F_5)=CFOR$	$C_2F_5CF(CF_3)CH(C_2F_5)C(O)F$
$C_2F_5CF(CF_3)C(CF_3)=C(CF_3)OR$	$C_2F_5CF(CF_3)CH(CF_3)C(O)CF_3$
$CF_3C(OR)=C(CF_3)C(CF_3)=C(OR)CF_3$	$CF_3C(O)CH(CF_3)CH(CF_3)C(O)CF_3$
	
	

If R_f^3 is a fluorine atom, the conjugate base of the fluorinated carbonyl compound will be a conjugate base of a fluoroalkyl acyl fluoride having the mesomeric structure:



5

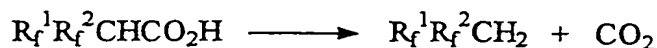
which, upon treatment with water, can yield an alpha-hydro fluoroalkyl carboxylic acid having the structure



- 10 Exemplary alpha-hydro fluoroalkyl carboxylic acids and their corresponding alkyl fluorovinylalkyl ether reactants are shown in the table below.

alkyl fluorovinylalkyl ether	fluorinated carbonyl compound
$CF_2=CFOR$	CHF_2CO_2H
$CFCI=CFOR$	$CHFCICO_2H$
$CCl_2=CFOR$	$CHCl_2CO_2H$
$CF_3CF=CFOR$	CF_3CHFCO_2H
$(CF_3)_2C=CFOR$	$(CF_3)_2CHCO_2H$

Many carboxylic acids are generally stable under neutral or acidic conditions, but may be decarboxylated under basic conditions to produce a hydrofluorocarbon:



5

Methods of decarboxylating secondary carboxylic acids are known in the chemical art. As an example of a suitable method, the addition of a stoichiometric amount of base (e.g., triethylamine) can be sufficient to cause decarboxylation and the production of a hydrofluorocarbon. Decarboxylation of fluoroalkyl carboxylates is described, for example, in *Chemistry of Organic Fluorine Compounds*, M. Hudlicky, pp. 496-500 (2nd ed. 1992).

As an alternative to decarboxylation, an alpha-hydrocarbonyl compound may be fluorinated to produce a more highly fluorinated or perfluorinated carbonyl compound. See, e.g., United States Patent No. 5,573,654 (Cheburkov et al.).

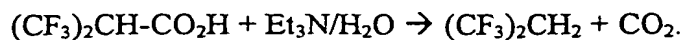
One specific embodiment of the process of the invention is the reaction of heptafluoroisobutenyl methyl ether with perfluorobutyl alkoxide to produce perfluorobutyl methyl ether and the conjugate base of alpha-hydro hexafluoroisobutanoyl fluoride; subsequently the conjugate base of alpha-hydro hexafluoroisobutanoyl fluoride can be hydrolyzed and then decarboxylated to form hexafluoropropane (HFC-236fa). The process can go specifically as follows:

First, heptafluoroisobutenyl methyl ether can be reacted with perfluorobutyl alkoxide according to the invention to produce perfluorobutyl methyl ether and the conjugate base of alpha-hydro hexafluoroisobutanoyl fluoride:



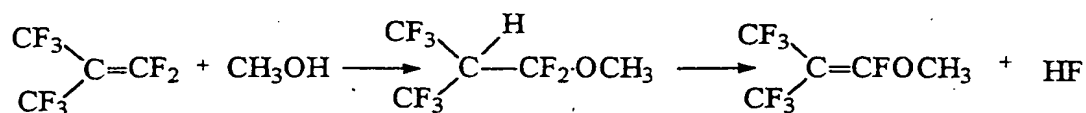
The perfluorobutyl alkoxide can be prepared in situ by contacting perfluorobutanoyl fluoride with anhydrous potassium fluoride as previously described. The perfluorobutyl methyl ether product can be easily separated from the non-volatile conjugate base, $(CF_3)_2C=CO^-FK^+$. The conjugate base may then be hydrolyzed to

its carboxylic acid, which can be decarboxylated with aqueous base to form hexafluoropropane:



5

In the above preferred reaction scheme, the heptafluoroisobutenyl methyl ether reactant can be obtained from a number of commercial sources, or can be prepared from perfluoroisobutene (PFIB). One method involves the addition of methanol to perfluoroisobutene to produce octafluoroisobutyl methyl ether, followed by dehydrofluorination of the octafluoroisobutyl methyl ether to produce heptafluoroisobutenyl methyl ether, as shown:



The alkoxylation (e.g., methoxylation, ethoxylation, etc., as desired) of perfluoroisobutene can be accomplished by methods known in the chemical art. One such method generally involves passing a gaseous stream containing perfluoroisobutene through methanol to produce octafluoroisobutyl methyl ether. The octafluoroisobutyl methyl ether can be dehydrofluorinated by any of a number of known methods, for example by refluxing the octafluoroisobutyl methyl ether in 15% aqueous potassium hydroxide at 100°C to produce heptafluoroisobutenyl methyl ether. An example of a procedure for producing heptafluoroisobutenyl methyl ether is described in Koshar R.H., Simmons T. C., Hoffman F.W., J Am. Chem Soc. 79 1741 (1957).

Thus, an embodiment of the invention includes the steps of providing perfluoroisobutene; reacting the perfluoroisobutene with methanol to produce octafluoroisobutyl methyl ether; dehydrofluorinating the octafluoroisobutyl methyl ether to produce heptafluoroisobutenyl methyl ether; reacting the heptafluoroisobutenyl methyl ether with a fluorinated alkoxide (e.g., perfluorobutyl alkoxide) to produce a hydrofluoroether and a conjugate base of the fluorinated carbonyl compound; hydrolyzing the conjugate base of the fluorinated carbonyl

compound to produce an alpha-hydro fluoroalkyl carboxylic acid; and decarboxylating the alpha-hydro fluoroalkyl carboxylic acid.

EXAMPLES

5 1. **Reaction of potassium pentafluoropropoxide with 1-methoxyheptafluoro-1-isobutene (methylheptafluoroisobutenyl ether).**

In a pressure glass reactor with magnetic bar stirrer, pentafluoropropionic acid fluoride (3.28 g, 75% purity 15 mmol) and potassium fluoride (1.27 g, 22
10 mmol) were heated in diglyme (8.7 g) for 30 min at 50° C, then held at 0° C for 1 hour then cooled to -50° C. Methoxyfluoroisobutene (7.51 g, 96% purity, 34 mmol) was added to the solution and the mixture agitated at room temperature for 17 hours.

After warming to 45°C, the reactor was vented into a trap (-78°C) and was
15 collected 0.23g of a mixture consisting of (GC%): 25% starting propionyl fluoride, 45.5% C₃F₇OCH₃, and 28% hexafluoropivaloyl fluoride CH₃C(CF₃)₂C(O)F (an isomerization product of the methoxyfluoroisobutene). The remaining contents of the reactor were distilled into a trap (-78C) under vacuum (25 torr at 40°C) to yield 6.39 g of a liquid consisting of (GC%): 36.5% C₃F₇OCH₃, 55% the
20 hexafluoropivaloyl fluoride and 3.5% starting vinyl ether.

To the diglyme residue in the reactor was added 10 ml H₂O (the solution had pH=4) and triethylamine (2.4g) to raise the pH to 8. Distillation yielded a fraction with b.p. up to 100°C, 1.59 g, which is mainly triethylamine with purity 85% contaminated 10% diglyme (triethylamine recovery 56%), and 3.25 g of
25 material which was recondensed in a second trap to give a 2.73g mixture (GC%): 87% CF₃CH₂CF₃, 8% CF₃CH=CF₂ (from dehydrofluorination), 2% C₃F₇OCH₃ and 1.5% CH₃C(CF₃)₂C(O)F (C5 acid fluoride).

The product yields were calculated based on weights of all obtained liquid and gaseous products mixtures, and purity of starting materials. Yield of
30 C₃F₇OCH₃, 86% on consumed pentafluoropropionic acid fluoride. Yield of CF₃CH₂CF₃, 50.1% and the hexafluoropivaloyl fluoride 49.5%.

2. **Reaction of isomeric potassium perfluorobutoxides with 1-methoxyheptafluoro-1-isobutene (methylheptafluoroisobutenyl ether).**

5 Using essentially the same procedure as in Example 1, an isomeric mixture of the perfluorobutyric acid fluorides (2.67 g with summary acyl fluorides content 81%, 10 mmol), potassium fluoride (0.78 g, 13 mmol), the 1-methoxyheptafluoro-1-isobutene (5.10 g, 96% purity, 23 mmol) was combined in 8.54 g diglyme and agitated at room temperature for 34 hours. The reactor was vented and 5.44 g of
10 material collected in the trap. The material consisted of (GC%): 4.0% starting C4 acyl fluoride, 35.3% $C_4F_9OCH_3$, 58.5% hexafluoropivaloyl fluoride (C5 acid fluoride) and a trace (0.4%) of diglyme. To the diglyme residue was added 8.64 g H_2O and 1.76 g triethylamine to yield 1.38 g $CF_3CH_2CF_3$ (after recondensation), and 95.5 % purity. The products yields were calculated based on the weight of
15 obtained mixtures, their GC% content and purity of starting compounds. Yield of $C_4F_9OCH_3$ is 77% (from perfluorobutyric acid fluorides and 85% on the consumed fluorides). Yield of $CF_3CH_2CF_3$ is 39% and C5 acid fluoride - 65%.

20 3. **Reaction of potassium pentafluoropropoxide with 1-ethoxyheptafluoro-1-isobutene (ethylheptafluoroisobutenyl ether).**

Using essentially the same procedure as in Example 1, pentafluoropropionyl fluoride (2.47g, 11 mmol), KF (0.94 g, 16 mmol) and 1-ethoxyheptafluoro-1-isobutene (4.26 g, 16.5 mmol) in 7.44 g diglyme were agitated at room temperature
25 for about 60 hours to yield 3.0 g of liquid consisting of (GC%): 80% $C_3F_7OC_2H_5$ and 5.5% starting vinyl ether. To the remaining diglyme solution was added equal volume of water and 1.8 g triethylamine (to pH 9) to yield 1.5 g of gas collected in the trap which comprised: 98 GC% $CF_3CH_2CF_3$ (including 10% of olefin $CF_3CH=CF_2$) plus 1% $C_3F_7OC_2H_5$. Triethylamine recovery (KOH addition to the
30 solution and distillation) gave 2.62 g liquid material, which consisted of: 2% $CF_3CH_2CF_3$, 58% triethylamine, 8% the unreacted starting ethoxyfluoroisobutene and 21% diglyme. Calculated yields by GC: $C_3F_7OC_2H_5$ 105% based on acid fluoride used; $CF_3CH_2CF_3$, 67% based on the consumed vinyl ether.

4. **Reaction of isomeric perfluorobutoxide mixture with 1-ethoxyheptafluoro-1-isobutene (ethylheptafluoroisobutenyl ether).**

Using essentially the procedure as in Example 1, a mixture of
5 perfluorobutyric acid fluorides (3.77 g with acyl fluoride content of 81%, 14 mmol),
KF (1.02 g, 17 mmol), the ethoxyisobutene (4.56 g with purity 88%, 0.18 mmol) in
8.33 g diglyme was agitated at room temperature for four days. The reactor was
vented to yield 0.67 g liquid which comprised (GC%): 88% starting acyl fluorides
mixture and 8% $C_4F_9OC_2H_5$. The reaction solution remaining in the reactor was
10 vacuum distilled to yield 3.0 g of a mixture which comprised (GC%): 75%
 $C_4F_9OC_2H_5$, 1.5% $C_2H_5C(CF_3)_2C(O)F$ and 7.6% starting vinyl ether. After
decarboxylation by treatment with triethylamine, the remaining diglyme solution
yielded 1.45 g $CF_3CH_2CF_3$ (purity 98% contaminated with 1.5% $C_4F_9OC_2H_5$ and
0.5% $(CF_3)CC_2H_5C(O)F$). Triethylamine recovery gave 2.5g organic liquid material
15 with b.p. up to 101°C, consisting of (GC%): 2.5% $CF_3CH_2CF_3$, 42% triethylamine,
9% starting vinyl ether and 29% diglyme. Calculated yields were: $C_4F_9OC_2H_5$, 72%
on the consumed acid fluoride mixture, $CF_3CH_2CF_3$, 75% on consumed vinyl ether.

20 5. **Reaction of 1-trifluoromethyl-perfluoro-3-pentanone with 1-methoxy-1-perfluoroisobutyl ether.**

Into a 500 ml three necked round bottomed flask equipped mechanical
stirrer, Friedrichs condenser, calcium sulfate drying tube and a thermometer was
placed anhydrous potassium fluoride (8.0g, 0.138 moles), anhydrous
25 diglyme(120g), Adogen™ 464 (0.3g), 1-trifluoromethyl-perfluoro-3-pentanone
(99.2% assay, 32.4g, 0.102 moles), and 1-methoxy-heptafluoroisobutylene (92%
assay, 25.4g, 0.11 moles). The light yellow heterogeneous mixture was stirred at
ambient temperature overnight after which time solids had formed on the sides of
the reaction flask. Heating to about 55°C was applied for two hours followed by the
30 gradual addition of water (50 ml) and triethylamine (12.0 gms, 0.119 moles). Some
outgassing occurred during the water addition and liquid products were noted and
collected in a -78°C cold trap which was attached after the condenser.

The mixture was heated to reflux temperature to collect the liquid hydrofluoroether in a Barrett trap and low boiling products in the dry ice trap. A total of 22.6 gms of product was collected in the Barrett trap which GC revealed as $C_2F_5CF(OCH_3)CF(CF_3)_2$, 79%. The molar yield of $C_2F_5CF(OCH_3)CF(CF_3)_2$ was calculated to be 50%. The condensate in the -78° cold trap, 19.0 gms, contained some additional $C_2F_5CF(OCH_3)CF(CF_3)_2$ (~6.%), $CF_3CH_2CF_3$ (44%) along with some starting vinyl ether. The presence of the some unreacted starting ketone was detected by gc/ms analysis. A 46% molar yield $CF_3CH_2CF_3$ was realized.

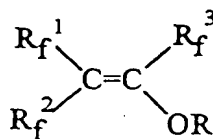
5

What is claimed is:

1. The reaction of a fluorinated alkoxide with an alkyl fluorovinylalkyl ether having alpha-beta carbon-carbon unsaturation relative to the ether oxygen, to produce a hydrofluoroether.

5

2. The reaction of claim 1, wherein the alkyl fluorovinylalkyl ether is of the formula:



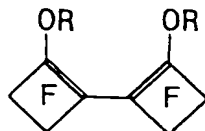
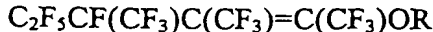
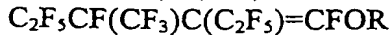
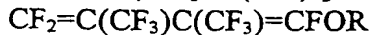
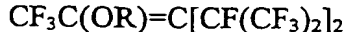
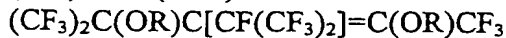
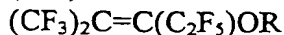
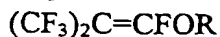
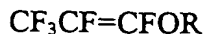
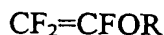
wherein R comprises an alkyl, and R_f^1 , R_f^2 , and R_f^3 are independently fluorine atoms or fluorinated aliphatics.

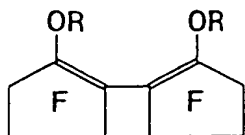
10

3. The reaction of claim 2, wherein R_f^1 , R_f^2 , and R_f^3 are each independently fluorine or a perfluorinated aliphatic having from 1 to 10 carbon atoms, and R is a linear or branched alkyl having from 1 to 6 carbon atoms.

15

4. The reaction of claim 1, wherein the alkyl fluorovinylalkyl ether is chosen from the group consisting of:





wherein each R independently comprises an alkyl.

5. The reaction of claim 1, wherein the fluorinated alkoxide has the general formula:

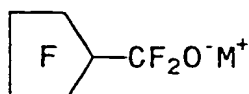
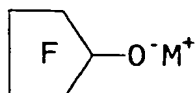
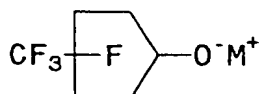
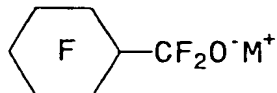
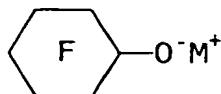
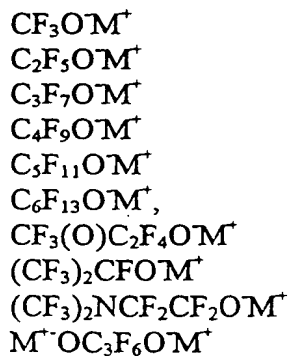


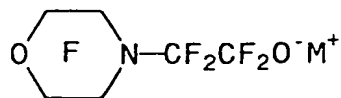
wherein R_f is a fluoroalkyl.

6. The reaction of claim 5, wherein R_f contains from 1 to 10 carbon atoms.

10

7. The reaction of claim 5, wherein the fluorinated alkoxide is chosen from the group consisting of



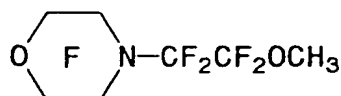
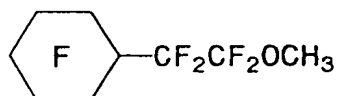
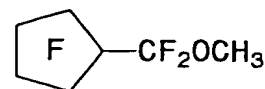
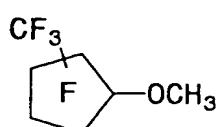
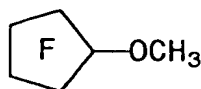
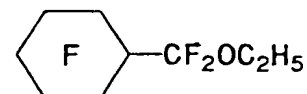
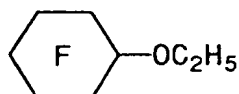
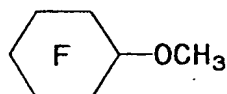


8. The reaction of claim 1, wherein the hydrofluoroether has the general formula $\text{R}_f\text{-O-R}$, wherein R_f is a fluoroalkyl having from 1 to 10 carbons, and R is an alkyl having from 1 to 6 carbons.

5

9. The reaction of claim 1, wherein the hydrofluoroether is chosen from the group consisting of $\text{C}_3\text{F}_7\text{OCH}_3$, $\text{C}_3\text{F}_7\text{OC}_2\text{H}_5$, $\text{C}_3\text{F}_7\text{OC}_3\text{H}_7$, $\text{C}_3\text{F}_7\text{OC}_4\text{H}_9$, $\text{C}_3\text{F}_7\text{OC}_5\text{H}_{11}$, $\text{C}_3\text{F}_7\text{OC}_6\text{H}_{13}$, $\text{C}_4\text{F}_9\text{OCH}_3$, $\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$, $\text{C}_4\text{F}_9\text{OC}_3\text{H}_7$, $\text{C}_4\text{F}_9\text{OC}_4\text{H}_9$, $\text{C}_4\text{F}_9\text{OC}_5\text{H}_{11}$, $\text{C}_4\text{F}_9\text{OC}_6\text{H}_{13}$, $\text{C}_5\text{F}_{11}\text{OCH}_3$, $\text{C}_5\text{F}_{11}\text{OC}_2\text{H}_5$, $\text{C}_5\text{F}_{11}\text{OC}_3\text{H}_7$, $\text{C}_5\text{F}_{11}\text{OC}_4\text{H}_9$, $\text{C}_5\text{F}_{11}\text{OC}_5\text{H}_{11}$, $\text{C}_5\text{F}_{11}\text{OC}_6\text{H}_{13}$, $\text{C}_6\text{F}_{13}\text{OCH}_3$, $\text{C}_6\text{F}_{13}\text{OC}_2\text{H}_5$, $\text{C}_6\text{F}_{13}\text{OC}_3\text{H}_7$, $\text{C}_6\text{F}_{13}\text{OC}_4\text{H}_9$, $\text{C}_6\text{F}_{13}\text{OC}_5\text{H}_{11}$, $\text{C}_6\text{F}_{13}\text{OC}_6\text{H}_{13}$, $\text{C}_7\text{F}_{15}\text{OCH}_3$, $\text{C}_7\text{F}_{15}\text{OC}_2\text{H}_5$, $\text{C}_7\text{F}_{15}\text{OC}_3\text{H}_7$, $\text{C}_7\text{F}_{15}\text{OC}_4\text{H}_9$, $\text{C}_7\text{F}_{15}\text{OC}_5\text{H}_{11}$, $\text{C}_7\text{F}_{15}\text{OC}_6\text{H}_{13}$, $\text{C}_8\text{F}_{17}\text{OCH}_3$, $\text{C}_8\text{F}_{17}\text{OC}_2\text{H}_5$, $\text{C}_8\text{F}_{17}\text{OC}_3\text{H}_7$, $\text{C}_8\text{F}_{17}\text{OC}_4\text{H}_9$, $\text{C}_8\text{F}_{17}\text{OC}_5\text{H}_{11}$, $\text{C}_8\text{F}_{17}\text{OC}_6\text{H}_{13}$, $\text{CF}_3\text{OC}_3\text{F}_6\text{OCH}_3$, $\text{C}_2\text{F}_5\text{OC}_2\text{F}_4\text{OC}_2\text{H}_5$, $\text{CH}_3\text{OC}_4\text{F}_8\text{OCH}_3$

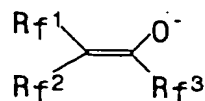
10



15

10. The reaction of claim 1, wherein a reaction product further comprises a conjugate base of a fluorinated carbonyl compound.

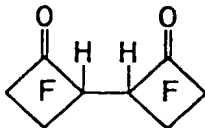
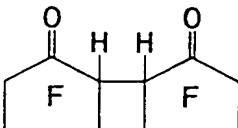
11. The reaction of claim 10, wherein the conjugate base of a fluorinated carbonyl compound has the mesomeric carbanion structure:



20

wherein R_f^1 , R_f^2 , and R_f^3 are independently fluorine atoms or fluorinated aliphatic groups.

12. The reaction of claim 10, wherein a conjugate acid of the fluorinated carbonyl compound can be a compound chosen from the group consisting of:

<chem>CHF2COF</chem>
<chem>CHFCICOF</chem>
<chem>CHCl2COF</chem>
<chem>CF3CHFCOF</chem>
<chem>(CF3)2CHCOF</chem>
<chem>(CF3)2CHC(O)C2F5</chem>
<chem>(CF3)2C(OR)CH[(CF(CF3)2)C(O)CF3]</chem>
<chem>CF3C(O)CH[CF(CF3)2]2</chem>
<chem>CF2=C(CF3)CH(CF3)COF</chem>
<chem>C2F5CF(CF3)CH(C2F5)COF</chem>
<chem>C2F5CF(CF3)CH(CF3)COCF3</chem>
<chem>CF3COCH(CF3)CH(CF3)COCF3</chem>



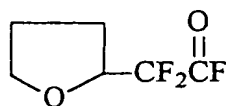
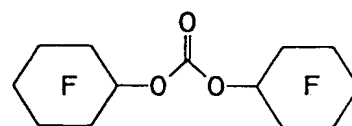
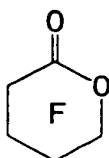
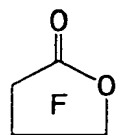
13. A process for preparing a hydrofluoroether, the process comprising the steps of:
- providing an alkyl fluorovinylalkyl ether;
- providing a fluorinated alkoxide;
- reacting the alkyl fluorovinylalkyl ether with the fluorinated alkoxide to produce a hydrofluoroether.

14. The process of claim 13, wherein the fluorinated alkoxide is provided from a fluorinated alkoxide precursor chosen from the group consisting of: a fluorinated acyl fluoride, a fluorinated acyl chloride, a fluoroalkyl ester, a

fluoroalkyl carbonate, a fluorinated ketone, a fluorinated tertiary alcohol, and a fluoroalkyl anhydride.

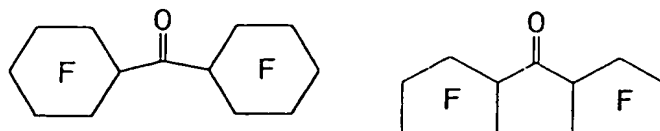
15. The process of claim 14, wherein the fluorinated alkoxide is
 5 provided by treating one or more fluorinated alkoxide precursors chosen from a fluorinated acyl fluoride, a fluorinated acyl chloride, a fluoroalkyl ester, a fluoroalkyl carbonate, or a fluoroalkyl anhydride with an anhydrous alkali metal fluoride in an anhydrous, polar, aprotic solvent to generate a fluorinated alkoxide.

- 10 16. The process of claim 15, wherein the fluorinated alkoxide precursor is chosen from the group consisting of $\text{CF}_3\text{C}(\text{O})\text{F}$, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{F}$, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{F}$, $\text{C}_4\text{F}_9\text{C}(\text{O})\text{F}$, $\text{C}_5\text{F}_{11}\text{C}(\text{O})\text{F}$, $\text{CF}_3\text{C}(\text{O})\text{Cl}$, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{Cl}$, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{Cl}$, $\text{C}_4\text{F}_9\text{C}(\text{O})\text{Cl}$, $\text{C}_5\text{F}_{11}\text{C}(\text{O})\text{Cl}$, $\text{CF}_3\text{CO}_2\text{CF}_3$, $\text{C}_2\text{F}_5\text{CO}_2\text{C}_2\text{F}_5$, $\text{C}_3\text{F}_7\text{CO}_2\text{C}_3\text{F}_7$, $\text{C}_4\text{F}_9\text{CO}_2\text{C}_4\text{F}_9$, $\text{C}_5\text{F}_{11}\text{CO}_2\text{C}_5\text{F}_{11}$, $\text{CF}_3\text{C}(\text{O})\text{-O-C}(\text{O})\text{CF}_3$, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{-O-C}(\text{O})\text{C}_2\text{F}_5$, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{-O-C}(\text{O})\text{C}_3\text{F}_7$, $\text{C}_4\text{F}_9\text{C}(\text{O})\text{-O-C}(\text{O})\text{C}_4\text{F}_9$, $\text{C}_5\text{F}_{11}\text{C}(\text{O})\text{-O-C}(\text{O})\text{C}_5\text{F}_{11}$, $\text{CF}_3\text{OC}(\text{O})\text{OCF}_3$, $\text{CF}_3\text{CF}_2\text{OC}(\text{O})\text{OCF}_2\text{CF}_3$, $\text{C}_3\text{F}_7\text{OC}(\text{O})\text{OCF}_3$,



17. The process of claim 14, wherein the fluorinated alkoxide is
 20 provided by treating a fluoroketone with an anhydrous alkali metal fluoride to generate a secondary fluoroalkoxide.

18. The process of claim 17, wherein the fluoroketone is chosen from the group consisting of CF_3COCF_3 , $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$, $\text{C}_3\text{F}_7\text{COC}_3\text{F}_7$, $\text{C}_4\text{F}_9\text{COC}_4\text{F}_9$, $\text{C}_4\text{F}_9\text{COCF}_3$, $\text{HC}_4\text{F}_8\text{COCF}_3$,



19. The process of claim 14, wherein the fluorinated alkoxide is provided by treating a fluorinated tertiary alcohol with a base to produce a fluorinated tertiary alkoxide.

5

20. The process of claim 19, wherein the fluorinated tertiary alcohol is chosen from the group consisting of $(\text{CF}_3)_3\text{COH}$, $(\text{CF}_3)_2\text{C}(\text{C}_2\text{F}_5)\text{OH}$, and $(\text{CF}_3)_2\text{CFCF}_2\text{C}(\text{CF}_3)_2\text{OH}$.

10 21. A process for preparing a hydrofluoroether, the process comprising the steps of:

providing octafluoroisobutylene;

reacting the octafluoroisobutylene to octafluoroisobutyl methyl ether by reaction with methanol;

15 dehydrofluorinating the octafluoroisobutyl methyl ether to form heptafluoroisobutenyl methyl ether;

reacting the heptafluoroisobutenyl methyl ether with a fluorinated alkoxide.

20 22. The process of claim 21, wherein the reaction product comprises a hydrofluoroether and a conjugate base of a fluorinated carbonyl compound.

23. The process of claim 22, further comprising the step of hydrolyzing the conjugate base of a fluorinated carbonyl compound.

25

24. The process of claim 23, further comprising the step of decarboxylating the hydrolyzed conjugate base of a fluorinated carbonyl compound to produce a hydrofluorocarbon.

25. The process of claim 24, wherein the hydrofluorocarbon comprises a hexafluoropropane.

5 26. A process for preparing a hydrofluoroether and a hydrofluorocarbon comprising the steps of
providing an alkyl fluorovinylalkyl ether;
providing a fluorinated alkoxide;
reacting the alkyl fluorovinylalkyl ether with the fluorinated alkoxide
10 to produce a hydrofluoroether and a conjugate base of a fluorinated carbonyl compound;
treating the conjugate base of a fluorinated carbonyl compound with water to produce an alpha-hydro carboxylic acid; and
decarboxylating the alpha-hydro carboxylic acid to form a
15 hydrofluorocarbon.

27. The process of claim 26, comprising the steps of:
providing heptafluoroisobutenyl methyl ether by reacting
perfluoroisobutene with methanol to produce octafluoroisobutyl methyl ether, and
20 dehydrofluorinating the octafluoroisobutyl methyl ether to produce heptafluoroisobutenyl methyl ether;
reacting the heptafluoroisobutenyl methyl ether with a fluorinated alkoxide to produce a hydrofluoroether and a conjugate base of a fluorinated carbonyl compound;
25 hydrolyzing the conjugate base of a fluorinated carbonyl compound to produce an alpha-hydro fluoroalkyl carboxylic acid; and
decarboxylating the alpha-hydro fluoroalkyl carboxylic acid to produce a hydrofluorocarbon.

30 28. The process of claim 27, wherein the hydrofluorocarbon comprises a hexafluoropropane.

INTERNATIONAL SEARCH REPORT

Internat'l Application No PCT/US 98/10437
--

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C41/14 C07C43/12 C07C41/01 C07C17/361 //C07C45/42,
C07C49/167, C07C49/457

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 38962 A (MINNESOTA MINING AND MANUFACTURING) 23 October 1997 see claims; examples	1-28
A	US 5 573 654 A (Y. CHEBURKOV) 12 November 1996 cited in the application see the whole document	26-28

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 October 1998

Date of mailing of the international search report

20/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Wright, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/10437

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9738962 A	23-10-1997	US 5750797 A	12-05-1998
US 5573654 A	12-11-1996	EP 0670294 A	06-09-1995
		JP 7309791 A	28-11-1995

Patent Number 5945552
Issue Date 1999 08 31
Appl. Data 975310 1997 11 21

Assignee AlliedSignal Inc.
Inventor(s) Puy, Michael Van Der

State/Country NY

Title Fluorinated vinyl oxiranes.

Abstract A compound having the formula: ##STR1## wherein: R is fluorine, hydrogen, an unsubstituted or substituted aliphatic or unsubstituted or substituted aromatic radical; R.sub.1 is an unsubstituted or substituted aliphatic radical, or unsubstituted or substituted aromatic radical; and R.sub.2 is hydrogen, an unsubstituted or substituted aliphatic radical, or unsubstituted or substituted aromatic radical.

Exmp. Claim 1

Ex Claim text A compound having the formula: ##STR4## wherein: R is fluorine, hydrogen, an unsubstituted or substituted aliphatic or unsubstituted or substituted aromatic radical; R.sub.1 is an unsubstituted or substituted aliphatic radical, or unsubstituted or substituted aromatic radical; and R.sub.2 is hydrogen, an unsubstituted or substituted aliphatic radical, or unsubstituted or substituted aromatic radical.

U.S. Class 549/563
IPC C07D 303/08
U.S. Refs 5328971 5481050

Other Refs M. Van Der Puy/Journal of Fluorine Chemistry 81 (1997) 187-191.
Chan et al., Organometallic Reactions in Aqueous Medium, Organometallic, vol. 9, No. 10, 1990, pp. 2649-2650.
Marshall, Additions of Organocopper Reagents to Vinyloxiranes, Chemical Reviews, 1989, vol. 89, No. 7, pp. 1503-1511.

Examiner Trinh, Ba K.
Agent Friedenson, Jay P.
Szuch, Colleen D.

Image Disc # This patent is on PatentImages disc# 1999\148 and PatentImages(chemical) disc# 1999\c59

Patent Number 5945493
Issue Date 1999 08 31
Appl. Data 099990 1998 06 19

Assignee E. I. du Pont de Nemours and Company
Inventor(s) Pechhold, Engelbert
Murphy, Peter Michael

State/Country PA

Title Fluorine-containing maleic acid terpolymer soil and stain
resists

Abstract A terpolymer having units of Formula I ##STR1## wherein X is
a C.sub.2-10 alkyl, C.sub.6-12 aryl, or C.sub.4-12 alkoxy
radical,
d is from about 3 to about 50,
R is a fluoroalkyl radical R.sub.f (A).sub.v --(B).sub.w --,
R.sub.f is a fully fluorinated straight or branched
aliphatic radical optionally interrupted by at least one
oxygen atom,
A is a divalent radical selected from --SO.sub.2 N(R")--,
--CON(R")-- , --S-- , or --SO.sub.2 -- , where R" is H, or a
C.sub.1-6 alkyl radical,
B is a divalent linear hydrocarbon radical -CtH.sub.2 t- ,
where t is 1 to 12,
Y is a divalent radical --CH.sub.2 --O-- ,
u, v, and w are each independently zero or 1,
R' is hydrogen or methyl,
e is from about 0.05 to about 10,
M is hydrogen, alkali metal, or ammonium, and
f is from about 5 to about 40,
and its use to provide soil resistance and resistance to
staining by acid dyes for fiber substrates is disclosed.

Exmp. Claim 1

Ex Claim text A composition comprising a terpolymer having units of
Formula I ##STR4## wherein X is a C.sub.2-10 alkyl,
C.sub.6-12 aryl, or C.sub.4-12 alkoxy radical,
d is from about 3 to about 50,
R is a fluoroalkyl radical R.sub.f --(A).sub.v --(B).sub.w
-- ,
R.sub.f is a fully fluorinated straight or branched
aliphatic radical optionally interrupted by at least one
oxygen atom,
A is a divalent radical selected from --SO.sub.2 N(R")-- ,
--CON(R")-- , --S-- , or --SO.sub.2 -- , where R" is H, or a
C.sub.1-6 alkyl radical,
B is a divalent linear hydrocarbon radical --C.sub.t
H.sub.2t -- , where t is 1 to 12,
Y is a divalent radical --CH.sub.2 --O-- ,
u, v, and w are each independently zero or 1,
R' is hydrogen or methyl,
e is from about 0.05 to about 10,
M is hydrogen, alkali metal, or ammonium, and
f is from about 5 to about 40.

U.S. Class 526/243 526/247 442/93
IPC C08F 12/30
U.S. Refs Re33365 3844827 3897206 4029867 4038027 4144026
4623683 4883839 5520962 5654068 5670246 5707708
5770656

Foreign Refs EPX 198903 0 306 992

Examiner Bell, James J.

Image Disc # This patent is on PatentImages disc# 1999\148 and
PatentImages(chemical) disc# 1999\c59

Patent Number 5929293
Issue Date 1999 07 27
Appl. Data 981391 1997 12 29

Assignee E. I. du Pont de Nemours and Company
Inventor(s) Krespan, Carl George
Petrov, Viacheslav Alexandrovich

State/Country DE

Title Process for the preparation of fluoroolefins

Abstract The invention concerns processes for the preparation of fluoroolefins, including a process for the deiodofluorination of an iodine containing fluorocarbon comprising contacting said iodine containing fluorocarbon with a fluoroolefin in the presence of an aluminum chlorofluoride catalyst.

Exmp. Claim 1

Ex Claim text A process for the deiodofluorination of an iodine-containing fluorocarbon comprising:
contacting an iodine-containing fluorocarbon with a fluoroolefin that is of the structure R.sub.f
"CF.dbd.CF.sub.2, wherein R.sub.f " is selected from the group consisting of F and CF.sub.3, in the presence of an aluminum chlorofluoride catalyst.

U.S. Class 570/153
IPC C07C 17/02
U.S. Refs 3192274 3377390 3557224 4073817 4587366

Foreign Refs GBX 197607 1 443 444
WOX 199506 WO 95/16656

PCT Number PCT/US96/10865 PCT Pub. Date 19970123
PCT Pub. No. WO97/02226 PCT Filing Date 19960625
PCT 371 Date 19971229 PCT 102 (e) Date 19971229

Related Data This application is a 371 of PCT/US96/10865 field Jun. 25, 1996 and a continuation of provisional application NO. 60/000,734 filed Jun. 30, 1995 .

Examiner Siegel, Alan
Image Disc # This patent is on PatentImages disc# 1999\123 and PatentImages(chemical) disc# 1999\c49

Patent Number 5922635
Issue Date 1999 07 13
Appl. Data 073528 1998 05 06
Inventor(s) Olah, George A.
Prakash, G. K. Surya

State/Country CA

Title Nanoscale solid superacid catalysts with pendant
fluoroalkylsulfonic acid or fluoro, perfluoroalkylsulfonic
acid groups

Abstract A solid superacid catalyst composition of a carrier material
having a particle size of between 0.5 and 5000 nm and at
least one pendant fluoroalkylsulfonic acid or fluoro,
perfluoroalkylsulfonic acid group attached thereto. Also,
methods for making this catalysts by attaching pendant
fluoroalkylsulfonic acid or fluoro, perfluoroalkylsulfonic
acid groups to the carrier material by various procedures to
form the catalyst composition.

Exmp. Claim 1

Ex Claim text A solid superacid catalyst composition comprising a carrier
material having a particle size of between 0.5 and 5000 nm
and at least one pendant fluoroalkylsulfonic acid or fluoro,
perfluoroalkylsulfonic acid group attached thereto.

U.S. Class 502/168 502/216 502/224 502/507 502/508 502/159 562/30
562/100
PC B01J 31/00 B01J 27/02 B01J 27/06 C07F 9/22
U.S. Refs 2732398 3920582 4044069 4547474 4697007 4721559
5179052 5220087 5288685 5294732 5336833 5571762
5648523

Related Data This application claims the benefit of Provisional
Application Ser. No. 60/046,338, filed May 7, 1997.

Examiner Bell, Mark L.
Agent Pennie & Edmonds LLP
Image Disc # This patent is on PatentImages disc# 1999\113 and
PatentImages(chemical) disc# 1999\c45



DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITE DE COOPERATION EN MATIERE DE BREVETS (PCT)

(51) Classification internationale des brevets ⁶ : C01B 21/086, 21/097, C07C 211/63, 211/64, 381/12, C07D 213/20, 213/26, 233/58, C07F 9/54, C08F 136/14, H01M 10/40, 6/16	A1	(11) Numéro de publication internationale: WO 99/40025 (43) Date de publication internationale: 12 août 1999 (12.08.99)
(21) Numéro de la demande internationale: PCT/CA99/00087 (22) Date de dépôt international: 3 février 1999 (03.02.99) (30) Données relatives à la priorité: 2,228,801 3 février 1998 (03.02.98) CA 2,256,945 18 décembre 1998 (18.12.98) CA (71) Déposants (pour tous les Etats désignés sauf US): ACEP INC. [CA/CA]; 75, boulevard René-Lévesque ouest, Montréal, Québec H2Z 1A4 (CA). CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE [FR/FR]; 3, rue Michel-Ange, F-75794 Paris Cedex 16 (FR). UNIVER- SITE DE MONTREAL [CA/CA]; Succursale Centre-Ville, C.P. 6128, Montréal, Québec H3C 3J7 (CA). (72) Inventeurs; et (75) Inventeurs/Déposants (US seulement): MICHOT, Christophe [FR/FR]; 8, rue Nicolas Chorier, F-38000 Grenoble (FR). ARMAND, Michel [FR/CA]; 2965 Fendall, Montréal, Québec H3T 1N2 (CA). GAUTHIER, Michel [CA/CA]; 237, rue St-Ignace, La Prairie, Québec J5R 1E6 (CA). RAVET, Nathalie [CA/CA]; 5279 McKenna, Montréal, Québec H3T 1T9 (CA).	(74) Mandataires: NADEAU, François etc.; Swabey Ogilvy Re- nault, Bureau 1600, 1981, avenue McGill College, Montréal, Québec H3A 2Y3 (CA). (81) Etats désignés: CA, JP, US, brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Publiée <i>Avec rapport de recherche internationale.</i> <i>Avant l'expiration du délai prévu pour la modification des</i> <i>revendications, sera republiée si des modifications sont</i> <i>reçues.</i>	
(54) Title: NOVEL MATERIALS USEFUL AS ELECTROLYTIC SOLUTES (54) Titre: NOUVEAUX MATERIAUX UTILES EN TANT QUE SOLUTES ELECTROLYTIQUES (57) Abstract The invention concerns novel ionic compounds with low melting point whereof the onium type cation having at least a heteroatom such as N, O, S or P bearing the positive charge and whereof the anion includes, wholly or partially, at least an ion imidide such as (FX ¹ O)N ⁻ (OX ² F) wherein X ¹ and X ² are identical or different and comprise SO or PF, and their use as solvent in electrochemical devices. Said composition comprises a salt wherein the anionic charge is delocalised, and can be used, inter alia, as electrolyte. (57) Abrégé La présente invention concerne de nouveaux composés ioniques de bas point de fusion dont le cation est de type onium possédant au moins un hétéroatome tel que N, O, S ou P portant la charge positive et dont l'anion inclut, en totalité ou en partie, au moins un ion imidure du type (FX ¹ O)N ⁻ (OX ² F) dans laquelle X ¹ et X ² sont identiques ou différents et comprennent SO ou PF, et leur utilisation comme solvant et dans des dispositifs électrochimiques. La composition comprend un sel dans lequel la charge anionique est délocalisée, et peut être utile, entre autre, comme électrolyte.		